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Proceedings of the 14th European Biomass Conference Biomass for Energy, Industry and Climate Protection

held in Paris, France, 17-21 October 2005

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BIO-BASED COMPOSITE MATERIALS FROM OLIVE STONE

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ABSTRACT: The present work describes the methodology used for the preparation and characterization of composite samples prepared by mixing various percentages of olive stone flour in a polyester resin matrix. A study on the chemical-physical properties of the olive stone is reported, as well as, a set of tests to evaluate the mechanical properties of the manufactured products obtained. Biodegradation studies were carried out on the obtained composite materials.
Keywords: Olive residues, Composites, Bio-materials.

1 INTRODUCTION

Olive oil extraction industry generates large amounts of residues. These by-products are formed, essentially, by a liquid effluent (vegetation water) and a solid residue composed by olive skin, stone, seed and water; usually designated by cake. The characteristics of the obtained cakes depend on the extraction process used, namely, they differ on the moisture content. Figure 1 presents a summary of the extraction processes used and the corresponding by-products. The stone extraction, in the two-phase process, is also indicated. The terminology press-cake, cake and sludges was used to distinguish the three types of solid residues. The press-cake is obtained from the traditional press process, the cake from the continuous three-phase process and the sludges from the continuous two-phase process. The moisture content of the press-cake, cake and sludges is, 27, 50 and 57 percent, respectively [1].

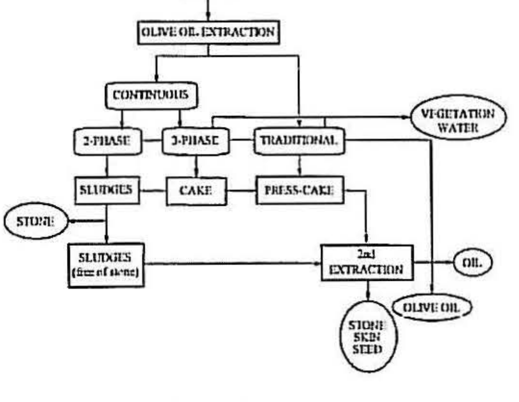

Figure 1. Olive oil extraction processes and related by-products.

Olive stone, a lignocellulosic material, is currently used mainly as energy source. Recently, we can found in the literature references to its use as a raw material to produce activated carbon [2] and furfural [3] and as heavy metal biosorbent [4]. Steam-explosion was also applied to this material in order to separate the main components: cellulose, hemicellulose and lignin [5].

Despite, the widely use of lignocellulosic materials as reinforcing agents or as fillers in polymer composites, we found in literature very few applications using olive stone. Both thermoset [6, 7] and thermoplastic [8] resins have been proposed to produce olive stone based composites.
The present work describes the methodology used for the preparation and characterization of composite samples prepared by mixing various percentages of olive stone flour in a polyester resin matrix. The effect of the olive stone content on the thermal properties of a composite material using a polyester resin as a matrix was evaluated. In addition, the incidence of accelerated aging effect on their properties was studied.

2 MATERIALS AND METHODS

2.1 Materials

The olive stone was supplied by an olive oil extraction plant (Azeites Milénium LDA, Mirandela, Portugal) and was obtained from a continuous two-phase process. It consists of a granular material (fragments with an average size of 2-5 mm) with a low contamination of skin and seeds (Figure 2). This material was grounded before use.

Figure 2. Sludges obtained from a 2-phase process (A), the extracted olive stone (B) and the residual sludges free of stone (C).

The polyester resin with a content of 41±2 percent of styrene (RESINMEX MR-227) and the methyl ethyl ketone peroxide (used as catalyst) were supplied by FIBROCENTRO (San José, Costa Rica). They were used as received.

2.2 Sample preparation

Samples were prepared by mixing different percentages

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Introduction

•Olive oil extraction industry generates a huge amount of residues. These by-products include a liquid effluent (vegetation water) and a solid residue formed by olive skin and stone. Figure 1 shows schematically the three processes currently used (traditional pressing process, continuous two phase process and continuous three phase process) and the corresponding residues.

•Olive stone is a lignocellulosic material mainly used as energy source.

•Some other applications have been proposed, such as production of activated carbon.

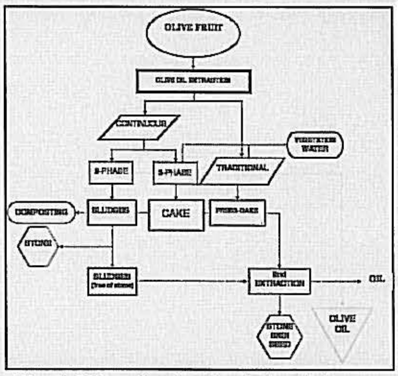
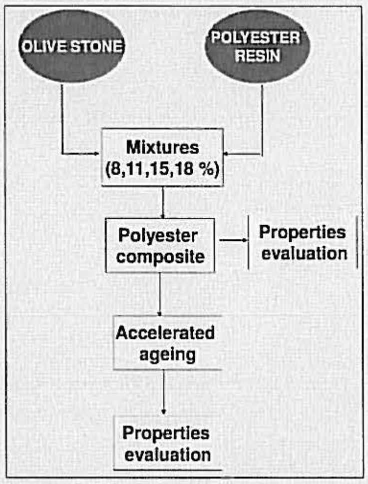


Fig. 1. Olive oil extraction industrial process

Olive stone could be used as a filler to make composite materials. Using natural materials, it is possible to make a low cost materials which can have a significant impact on environment.

Experimental



•The biodegradation of composite materials biodegradation of the samples was studied using soil with a mixed culture of *gloeophyllum trabeum* fand *phanerochaetes crysosporium* (50% each).

•Samples were incubated at 30 ºc for 30 days and observed diary and control the colonization of the micelio on the polyester, following a methodology similar to that of Ferreira da silva (9)

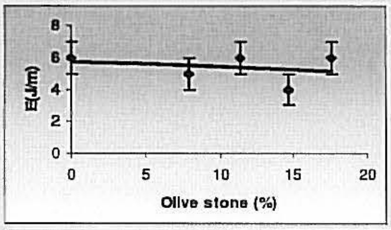
Results

Proximate analysis of Olive Stone residues

Analysis	Method ASTM	Results
% Humidity	D1102	8,06
% Ash	D1102	0,52
%Ciclohexane etanol extracts	D1107	2,1
% Cold water solubility	D1110	1,50
% Holocellulose	D1104	71,53
% lignin	D1106	55,8
Density (g/cm³)	D 792	1,67

Density of composite materials

Olive Stone (%)	Density (g/cm³)	
	No ageing	192 hrs. ageing
0	1,25	0,82
8	1,24	1,08
11	1,24	0,83
15	1,20	1,12
18	1,22	1,22



Effect of the content of seed of olive in the resistance to the impact

Amount of CO_2 produced during the assay

Olive stone (%)	% degradation	m moles CO_2 produced	
		15 days	30 days
0	0	0,10	0,40
11	10	0,45	0,85
15	20	0,50	0,85
18	20	0,60	0,90

Glass transition temperature (Tg) of polyesters reinforced, to the being put under 192h of aging

Olive Stone (%)	Tg (°C)	
	No ageing	192 hrs. ageing
0	88	114
8	91	117
11	90	105
15	85	102
18	89	103

Temperature media of decomposition (Tdm) of polyesters reinforced with different percentage from pressed olive stone

Olive stone (%)	Tdm (°C)	
	No ageing	192 hrs ageing
0	404	395
8	409	405
11	381	408
15	386	406
18	382	406

Degradating inoculum of of *G. trabeum* and *P. chrysosporium and P.ostreatus*

Olive Stone (%)	t_0	$t_{15\ days}$	t_{30days}
11	A_{280}	-	A_{254}
11	-	-	A_{254}, A_{280}
15	A_{280}	-	-
15	A_{280}	A_{254}	A_{280}, $A_{310.A254}$
18	-	A_{254}	A_{310}, A_{352}
18	-	A_{254}	A_{280}, $A_{310.A254}$

Conclusions

The experimental results show composite materials with a heterogeneous distribution with matrix, reason for which the properties exhibited by these materials are not good enough to be used in the plastic making industry. Nevertheless, it is important to mention that these materials, although do not reinforce the matrix can be used like fillings in order to contribute with the environmental diminution produced by them. It is necessary to carry on further studies to obtain a more homogeneous material in order to study the effect of the olive stone content in their mechanical properties.

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